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Photoemission and Thermal Desorption Studies of Electron Beam

Polymerized Thiophene Films on Pt(111)

by

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Surface Science, in press

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ABSTRACT

We report on the investigation of electron beam induced modifications of thin films (on the order of a few monolayers) of thiophene adsorbed on Pt(111). X-ray and ultraviolet photoelectron spectroscopy have been used to characterize the growth and thermal behavior of these thin films upon electron beam irradiation. These films show characteristics that are consistent with electron beam induced polymerization. Upon electron beam modification there is a broadening of all peaks in the UPS spectra which is attributed to the delocalization of electrons due to increased interaction between aromatic rings. XPS and UPS spectra show changes that parallel growth of a polymer, as observed for thiophene oligomers and, exhibit the same spectral features that are reported in the literature for electrochemically grown films (1000 Å) of polythiophene. In addition to spectral changes, one would expect polymerization to create changes in the behavior of the material as well. In comparing the behavior with annealing of the unmodified thiophene, with that of the electron beam modified thiophene, we find dramatic differences. At 234 K unmodified thiophene exhibits loss of the multilayer and by 340 K is decomposed. In contrast, the beam modified thiophene does not show a loss of material with annealing, and retains its intact character even at elevated temperatures (600 K). The changes observed in the XPS and UPS spectra of thin thiophene films are consistent with electron beam polymerization.

**Photoemission and Thermal Desorption Studies of Electron
Beam Polymerized Thiophene Films on Pt(111)**

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Surface Science in press, 1992

Abstract

We report on the investigation of electron beam induced modifications of thin films (on the order of a few monolayers) of thiophene adsorbed on Pt(111). X-ray and ultraviolet photoelectron spectroscopy have been used to characterize the growth and thermal behavior of these thin films upon electron beam irradiation. These films show characteristics that are consistent with electron beam induced polymerization. Upon electron beam modification there is a broadening of all peaks in the UPS spectra which is attributed to the delocalization of electrons due to increased interaction between aromatic rings. XPS and UPS spectra show changes that parallel growth of a polymer, as observed for thiophene oligomers and, exhibit the same spectral features that are reported in the literature for electrochemically grown films (1000Å) of polythiophene. In addition to spectral changes, one would expect polymerization to create changes in the behavior of the material as well. In comparing the behavior with annealing of the unmodified thiophene, with that of the electron beam modified thiophene, we find dramatic differences. At 235K unmodified thiophene exhibits loss of the multilayer and by 350K is decomposed. In contrast, the beam modified thiophene does not show a loss of material with annealing, and retains its intact character even at elevated temperatures (600K). The changes observed in the XPS and UPS spectra of thin thiophene films are consistent with electron beam induced polymerization.

I. Introduction

The search for new materials that take advantage of the variable properties of plastics and combine them with the electrical conductivity of metals has lead to the development of many interesting conducting polymers [1,2]. Organic conducting polymers such as the five membered heterocyclic compounds are of great interest due to their electronic properties and their inertness to many solvents [8]. Many of these polymers may be made highly conducting upon doping (10^{-8} to 10^{+2} ohms cm^{-1}) [3,4,5]. These doped organic polymers are also part of a new class of materials that exhibit nonlinear optical properties. These properties make their use in a wide range of technological applications possible [6].

It is known that the electronic properties of organic polymers depend on the degree of order present in the polymeric chains [1,3,4]. Much of the work done on conducting polymers, such as polythiophene, has been done on electrochemically grown films on the order of 500-1000Å thick [7-10]. Our study focuses on the use of a single crystal metal surface as a substrate to generate a thin film of thiophene monomer, which we propose can be polymerized by use of an electron beam. Electron beam polymerization would allow for controlled polymerization of very small areas. With the use of a single crystal substrate it is our hope that we can increase the degree of order in the polymer films and thus realize a greater degree of control of the electronic properties and open the possibility to new uses.

II. Experimental

Experiments were conducted on a VG Scientific ESCALAB MKII surface analysis system under ultra high vacuum conditions with a base pressure of 1×10^{-10} mbar. XPS spectra were obtained using $\text{MgK}\alpha$ radiation (1253.6eV)

with analyzer pass energies of 10 and 20eV. A Shirley type non-linear background subtraction was utilized to obtain peak areas. UPS spectra were obtained with HeI radiation (21.2eV). The sample was biased at -7.0V to remove interference from the spectrometer secondaries during UPS experiments. Experiments were performed on a Pt(111) crystal that was cleaned by argon bombardment, heated to 600C in 1×10^{-6} Torr of oxygen for several minutes, and then annealed to 1000C. This was repeated until no traces of contaminants could be detected by XPS. It was found that oxygen treatments were sufficient to remove carbon and sulfur between thiophene experiments.

Thiophene was used as obtained from the Aldrich Chemical Co. with a purity of 99+%. The vapor pressure of thiophene at room temperature is 80 Torr which allows the use of a gas line for dosing. A vial of thiophene was connected to the gas line which goes to a directional doser with a 2u pin hole. The doser can then be positioned directly in front of the sample in the main analysis chamber. Several freeze-pump-thaw cycles were performed to reduce air and water vapor from the vial before dosing. The doser was then calibrated by comparison with thiophene backfilling experiments. The sample was cooled to 145K where we found that an exposure of 5L was sufficient to grow a multilayer.

Terthiophene crystals of 99% purity were used as received from the Aldrich Chemical Co. A thin film (macroscopic) of terthiophene on a Pt(111) crystal was prepared by dissolving the crystals in methanol and letting the solvent evaporate. Experiments utilizing terthiophene were conducted at room temperature.

Electron beam modification was accomplished by use of the VG LEG 51 electron flood gun which supplies 500eV electrons. Electron beam doses were

determined by measurement of the current to the sample. During electron beam treatment, the sample was maintained at 145K and exposed to electron beam currents of 20 - 70ua for 2-25 min.

III. Results

A. Thiophene Film Growth

Thiophene film growth was monitored by XPS and UPS techniques. At an exposure of 1.3L there are two well defined S2p XPS peaks as shown in figure 1a. The binding energy of the S2p_{1/2} and the S2p_{3/2} are 164.9 and 163.8eV and are represented in the correct ratio of 1:2. At 2.7L, figure 1b, the S2p peaks are no longer resolved and there is a shoulder developing at high binding energy. The increased intensity at higher binding energy signals the onset of multilayer growth. By 5.3L, the shoulder seen at 2.7L has grown to dominate the spectra at higher binding energy (fig. 1). Remnants of a shoulder at low binding energy remain, which we believe corresponds to the first layer of thiophene. The first layer is different than the multilayer due to enhanced interaction with the substrate. In very thin films this leads to a convolution of the two types of thiophene peaks as seen in figure 1. The carbon 1s data shown in figure 2 follows the same trend with a binding energy of 284.5eV at a 1.3L exposure, shifting upward with increasing exposure to 285.0eV at 5.3L. There are no further changes in the shape or binding energy of the S2p or C1s spectra at this temperature with further exposure. Growth of the thiophene film can also be monitored as the evolution of the ratio of the integrated area of the S2p versus area of the Pt 4f peaks as a function of exposure. The S/Pt ratio shows a steady increase with exposure until 5.3L above which there is no change with further exposure as seen in figure 3. It should be noted that the

C/S ratio remains approximately 4:1 during the exposure, as expected for thiophene.

Figures 4a-e show UPS spectra with increasing exposure to thiophene. At exposures up to 1.3L the Pt peak shape dominates the spectra. With increased exposure the thiophene features between 4-14eV are seen to develop and dominate the spectra while the Pt features at 0-5eV are diminished. Work function measurements (obtained from the shift in the secondary electron onset in the UPS spectra) are shown in figure 5. The work function changes with increasing exposure until 5.3L, after which there are no changes indicating that the monolayer is complete and multilayer growth occurs.

One can compare the UPS spectra for condensed unmodified thiophene, shown in figure 4e, with the gas phase spectra found in reference 15. This can be accomplished by shifting the gas phase spectra by 5eV to lower binding energy to correct for the change in reference level from the vacuum level to the Fermi level of the Pt substrate. In doing this we find the UPS spectra of condensed thiophene and the gas phase spectra to be the same with the exception of some expected broadening due to solid state effects. The two spectra exhibit the same features in the same relative positions. From this comparison we can conclude that we have a film of condensed, intact thiophene on the surface.

B. Temperature Dependence of Unmodified Thiophene

The S2p and C1s XPS spectra, in figures 6 and 7, show the evolution of thin unmodified condensed thiophene films on Pt with annealing from 145K to 600K. When unmodified thiophene is annealed to 235K the S2p_{1/2} and 2p_{3/2} XPS peaks shift from 165.7 and 164.6 eV to 164.8eV and 163.7eV with a shoulder at 162.0eV as shown in figure 6b. It is at this temperature that the S/Pt ratios, shown in figure 8, show a large decrease, a factor of 3, indicating a loss

of material. By 350K the S2p peak (fig. 6d) exhibits a shift of 2.6eV to lower binding energy and there is no further change in the binding energy upon further annealing up to 800K. The C1s spectra shown in figure 7 exhibits shifts to lower binding at the same temperatures. Upon annealing to 235K the C1s peak (fig. 7 b) shifts from 285.0eV to 284.4eV. By 350K (fig. 7 d) the C1s peak center has shifted to 284.0eV.

UPS annealing experiments (spectra in figure 9) also show changes at the same temperatures as in the XPS annealing experiments. Annealing to 235K (fig 9b) shows greatly diminished thiophene peaks from 4 to 14eV, and increased intensity of the Pt substrate peaks noted most clearly near the Fermi level (E_f) between 0 and 5eV. This effect indicates that a large loss of material occurs by 235K, but that the thiophene that remains on the surface is still intact, as shown by the presence of the correct thiophene peaks. UPS anneal spectra for temperatures greater than 300K (fig 9c-f) no longer resemble that of thiophene, the peaks have diminished and shifted away from the values observed for thiophene (fig 9a and ref 15). This indicates that major structural changes have occurred by 300K. Work function measurements presented in figure 10 show changes between 235K and 300K, the same temperature range where changes are observed in the XPS and UPS spectra.

C. Electron Beam Induced Modification

Exposures of 5.3L of thiophene at 145K were subsequently exposed to 500eV electrons from the flood gun. Currents of 30ua were supplied to the sample for 20 minutes which provides a dose of 3.5×10^{17} electrons/cm². XPS and UPS were then used to monitor the surface species.

After modification, the S2p XPS peak broadens and shifts to lower binding energy as shown in figure 11b. The peak center is now at 163.4eV with a high binding energy shoulder at 164.4eV and a low binding energy shoulder at

162.3eV. This corresponds to a shift of 1.3eV of the main sulfur peak upon modification. The C1s spectra shown in figure 12b follows the same trend of broadening and shifting to lower binding energy, moving from 285.0eV to 284.3eV.

After electron beam modification UPS spectra show a broadening of all peaks. With increased electron beam modification the features in the 6-10eV region become broader and less distinct, and the features in the 1-6eV region dominate the spectra (fig 13b). Also from the UPS spectra, we note that the work function increased by 1.5eV upon modification, which is consistent with the formation of a higher electron density species on the surface.

D. Temperature Dependence of Beam Modified Thiophene

After electron beam treatment of thin thiophene films, the changes observed in the XPS and UPS spectra upon annealing, are much different than for unexposed thiophene films. In figure 13 the UPS spectral shape does not change on annealing from 145K (fig 13b) to 600K (fig 13c 500K). Work function measurements presented in figure 10 show no change in the beam modified material work function upon annealing from 145K to 600K. XPS results show the same increased stability for the beam modified material at elevated temperatures. The S2p XPS spectra as a function of temperature in figure 11, show the major sulfur peak remains at 163.4eV until 600K. We see the development of a peak at 162.3eV after annealing to 400K (fig 11d). This peak may be due to decomposition of residual unmodified material or slight decomposition of some of the polymer upon annealing. It is clear, however, that significant intensity of the XPS S2p peak remains at high binding energy (163.4 and 164.4 eV) well above 350K, and indeed all the way up to and above 600K. This behavior is very different than what we see for unmodified thiophene, the XPS S/Pt peak area ratios of the beam modified film remain constant showing

no loss of material up to 600K. The apparent formation of this thermally more stable material is consistent with polymerization of thiophene upon exposure to electron beam irradiation.

IV. Discussion

Our XPS and UPS results show that there are significant differences between electron beam modified and unmodified thiophene. Our results are consistent with electron beam irradiation induced polymerization of the thin thiophene films. In support of this, we compare our results given above with work in the literature on electrochemically grown thiophene films, terthiophene, and theoretical treatments of polymerization.

Electron beam irradiation of thin thiophene films produces significant changes in the XPS and UPS spectra. Upon electron beam modification (3.5×10^{17} electrons/cm²) one observes a broadening of all peaks in the UPS spectra. By comparing the spectra of terthiophene (fig 13d) to thiophene (fig 13a) one can see what changes are expected in the UPS spectra upon formation of the polymer. It is useful to compare the beam modified spectra with that of terthiophene, since the trimer, terthiophene, is known to have the same fundamental structure as polythiophene [1]. In comparing the spectrum of beam modified thiophene (fig 13b) with that of terthiophene (fig 13d) one sees a striking similarity of the two spectra. In comparing the terthiophene spectrum with that of thiophene the major difference is that the peaks in the 5-10eV region are broader and less distinctive for terthiophene than for thiophene. The spectrum of the beam modified thiophene continues this trend with the peaks in the 5-10eV range now hardly discernible. From this, in addition to the XPS experiments, one can conclude that the basic integrity of the molecular unit is

maintained during electron beam modification, and that the species formed has a similar structure to terthiophene.

Polymerization is expected to produce increased interaction between the molecules which gives rise to delocalized electronic states. It is useful to look to the literature to see what effects polymerization is expected to have on the XPS and UPS spectra, and compare what is seen to our spectra of beam modified thiophene.

Delocalization of electrons in the valence levels produces a relaxation in the core levels, this is expected to show up as a shift of the XPS peaks to lower binding energy. Figures 11b and 12b show that the main S2p and C1s peaks have broadened and shifted by 1.3eV and 0.7eV to lower binding energy with electron beam modification. These spectral changes are consistent with the trend to shift to lower binding energy and broaden with increased number of interacting rings as predicted by theory [3], and observed by Tourillon [7,8] for the sequence from monomer to polymer. Our beam modified S2p_{3/2} binding energy of 163.4eV is very close to the value of 163.8eV reported by Tourillon for electrochemically grown films of polymethylthiophene.

Polymerization and delocalization of electrons produces the most dramatic changes in the UPS spectra. To better understand the valence band spectra of polythiophene Tourillon and Jugnet [7] have followed the evolution of the UPS spectra of condensed thiophene, condensed bithiophene and condensed terthiophene, and compared the results to their electrochemically grown films (1000Å). They find that the UPS spectra of the deeper lying orbitals (4-14eV) are unchanged for the series from the monomer to the polymer, with the exception of broadening, and the formation of a new band near 3eV that extends down to 1eV with increasing number of aromatic rings. It is more difficult to distinguish the thiophene features in our thin films due to lower

contribution of thiophene to the total signal compared to the thicker electrochemically grown films. This is especially true in the region of 0-4eV where the Pt d band features are located. However, it is still possible to make useful general comparisons between the two spectra. Comparison of our UPS spectra of beam modified thin thiophene films with their electrochemically grown thick film of poly-3-methylthiophene shows that both exhibit the same basic structure and, most importantly, prominence of the features from 1-3eV.

The observation of the band to the low binding energy side of the pi-bonding peak at 4eV is nicely corroborated by theory. Theoretical calculations [3], including CNDO/S3 [2,11], and valence effective Hamiltonian (VEH) [4] models for five membered heterocycles, predict the appearance of an extended pi-bonding band in the UPS spectra upon polymerization. This band at about 2eV (just to the low binding energy side of the pi-bonding peak) is attributed to the extension of the pi-bonding orbitals from delocalization of electrons due to the interaction between aromatic rings. The existence of this band in our beam modified material (fig 13b), as predicted by theory, implies that a species with some degree of order exists. Our XPS and UPS analysis agrees with theory and experiments in that we see the evidence of an extended pi-bonding band between 1-3eV (fig 13b), and broadening of the features at 5-10eV which is consistent with electron beam irradiation induced polymerization in thin thiophene films.

We expect polymerization to create changes in the behavior of the material as well as the spectra changes discussed above. In comparing the behavior with annealing of unmodified thiophene with that of electron beam modified thiophene we find dramatic differences.

We used exposures of 5.3L at 145K to generate a thin film of thiophene, a few monolayers, as discussed in the film growth section. We then monitored the

behavior of this unmodified thiophene film upon annealing from 145K to 600K. After annealing to 235K, both XPS (fig 8) and UPS (fig 9b) spectra show a decrease in the thiophene signal due to loss of material, which is attributed to loss of the multilayer. Indeed, XPS (fig 6b) and UPS (fig 9b) spectra upon annealing to 235K closely resemble those obtained after exposure to 1.3L of thiophene at 145K (figs 1a and 4b).

Substantial changes in the peak shapes and energies are observed in both XPS (fig 6d, 7d) and UPS (fig 9c-f) spectra after annealing the unmodified thiophene film to 350K. Annealing to higher temperatures did not result in any further shifts of the S2p peaks. Work function measurements, shown in figure 10, also indicate major changes occur in the surface species between 235K and 350K. The appearance of the S2p_{3/2} peak (fig 6d) at 162.0 eV above 350K in condensed unmodified thiophene indicates cleavage of the C-S bond and the formation of a surface sulfide species [12]. This decomposition is also seen by others, who have noted that the multilayer has desorbed by 235K leaving a monolayer film of intact thiophene, and that by 350K thiophene is decomposed [9,12-14].

One can now compare the behavior of unmodified thiophene and electron beam modified thiophene with annealing. In contrast to the unmodified thiophene, the beam modified material does not show a loss of material and decomposition upon annealing as shown by XPS and UPS results. The beam modified UPS anneal spectra shown in figure 13b, c show no changes in the spectral shape upon annealing up to 600K. UPS work function measurements, shown in figure 10, reflect the observed stability in that the beam modified material shows no change in work function with annealing. The major S2p peak of the beam modified thiophene, shown in figure 11b, remains at 163.4eV, well above the surface sulfide value, until 600K. At 400K we see a shoulder

growing in at 162.3eV. This growth of the 162.3eV peak may be due to decomposition of the unmodified material or some decomposition of the polymer with annealing. It is worth noting that the high binding energy peaks at 164.4eV and 163.4eV remain strong at elevated temperatures indicating that a species with increased thermal stability has been formed by beam modification. This is also evident in the stability of the C/S and S/Pt peak area ratios with annealing. Annealing the beam modified material from 145K to 600K produces little change in the S/Pt ratio as seen in figure 8. The above results show the beam modified material to be more thermally stable to loss of material and decomposition than unmodified thiophene. These changes produced by beam modification are consistent with electron beam induced polymerization.

Our XPS and UPS results all show major differences between unmodified and electron beam modified thiophene films on Pt(111), and that these differences are consistent with polymerization of thiophene upon exposure to electron beam irradiation. Analysis and comparison of our XPS and UPS results for beam modified thiophene with what is known about polythiophene and its derivatives in the literature offers support for our conclusions of electron beam induced polymerization of thiophene.

Summary

1. The effect of delocalization of electrons upon beam modification is seen as shifts to lower binding energy in the S2p (fig 11b) and C1s (fig 12b) XPS peaks. This trend is consistent with results by Tourillon [7,8] on a series of thiophene oligomers.
2. Upon beam modification we see that the peaks in the 5-10eV region are broader and less distinctive and the features in the 1-4eV region dominate in the UPS spectra (fig 13b). These spectral changes are consistent with the

formation of an extended pi-bonding band which is predicted by theory and is explicitly attributed to increased interaction of aromatic rings [2-4,11]. These trends are corroborated by experiments of known polythiophene derivatives [7,8], are seen in our UPS spectra of terthiophene (fig 13d) and were observed for electrochemically grown films of polythiophene [7,8].

3. Increased thermal stability of the beam modified material as seen by XPS and UPS indicates formation of a more stable surface species. This is evident in that the beam modified material shows no loss of the multilayer at 235K and remains more stable with annealing to 600K (figs 8,10,11,12 and 13). This is consistent with behavior expected upon polymer formation.

Our experimental results correlate well with theory and experiments on thiophene oligomers and electrochemically grown films. This agreement provides evidence supporting our conclusions that electron beam modification of thin films of thiophene induces polymerization.

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Figure Captions

Figure 1. Sulfur 2p region of the XPS spectrum following various exposures of thiophene to the Pt(111) sample. Thiophene exposures in Langmuir are indicated for each spectrum.

Figure 2. Carbon 1s region of the XPS spectrum following various exposures of thiophene to the Pt(111) sample. Thiophene exposures in Langmuir are indicated for each spectrum.

Figure 3. Ratio of the sulfur 2p to Pt 4f peak areas as a function of thiophene exposure (Langmuir) to the Pt(111) sample.

Figure 4. He I ultraviolet photoelectron spectra as a function of thiophene exposure to the Pt(111) sample. Exposures are given in Langmuir units.

Figure 5. Change in the sample work function, from the onset of the UPS spectra, as a function of thiophene exposure (Langmuir) to the Pt(111) sample. The circles and squares represent two separate experiments.

Figure 6. Sulfur 2p region of the XPS spectrum of multilayer of unmodified thiophene film on Pt(111) following annealing to higher temperature. a) Multilayer film at 150K. b) after annealing sample to 235K c) after annealing sample to 300K d) after annealing sample to 350K e) after annealing sample to 400K.

Figure 7. Carbon 1s region of the XPS spectrum of multilayer of unmodified thiophene film on Pt(111) following annealing to higher temperature. a) Multilayer film at 150K. b) after annealing sample to 235K c) after annealing sample to 300K d) after annealing sample to 350K e) after annealing sample to 400K.

Figure 8. Ratio of the sulfur 2p to Pt 4f integrated area after multilayer thiophene film deposition followed by annealing to the indicated temperature. The circles show the change in the ratio of the unmodified thiophene film. The dashed line has been added as a guide to the eye. The triangles, squares and crosses are from three separate experiments and show the stability of the electron beam modified film with annealing.

Figure 9. He I ultraviolet photoelectron spectra of unmodified thiophene films following annealing at the indicated temperatures.

Figure 10. Change in the sample work function, from UPS onset, of electron beam modified and unmodified thiophene films following annealing to the indicated temperatures. The crosses represent the electron beam modified thiophene film. The circles represent the unmodified thiophene film. (The data have been normalized at 0.0eV).

Figure 11. Sulfur 2p region of the x-ray photoelectron spectra showing the thiophene multilayer (a), changes occurring upon beam modification (b) and the electron beam modified layer after annealing to the indicated indicated temperatures (c-f).

Figure 12. Carbon 1s region of the x-ray photoelectron spectra showing the thiophene multilayer (a), changes occurring upon beam modification (b) and the electron beam modified layer after annealing to the indicated temperatures (c-f).

Figure 13. He I ultraviolet photoelectron spectra showing the changes that occur in the thin thiophene film upon electron beam modification. a). Thin unmodified thiophene film. b) Electron beam modified thiophene film. c) Electron beam modified thiophene film upon annealing to 500K. d) Film of terthiophene for comparison purposes.

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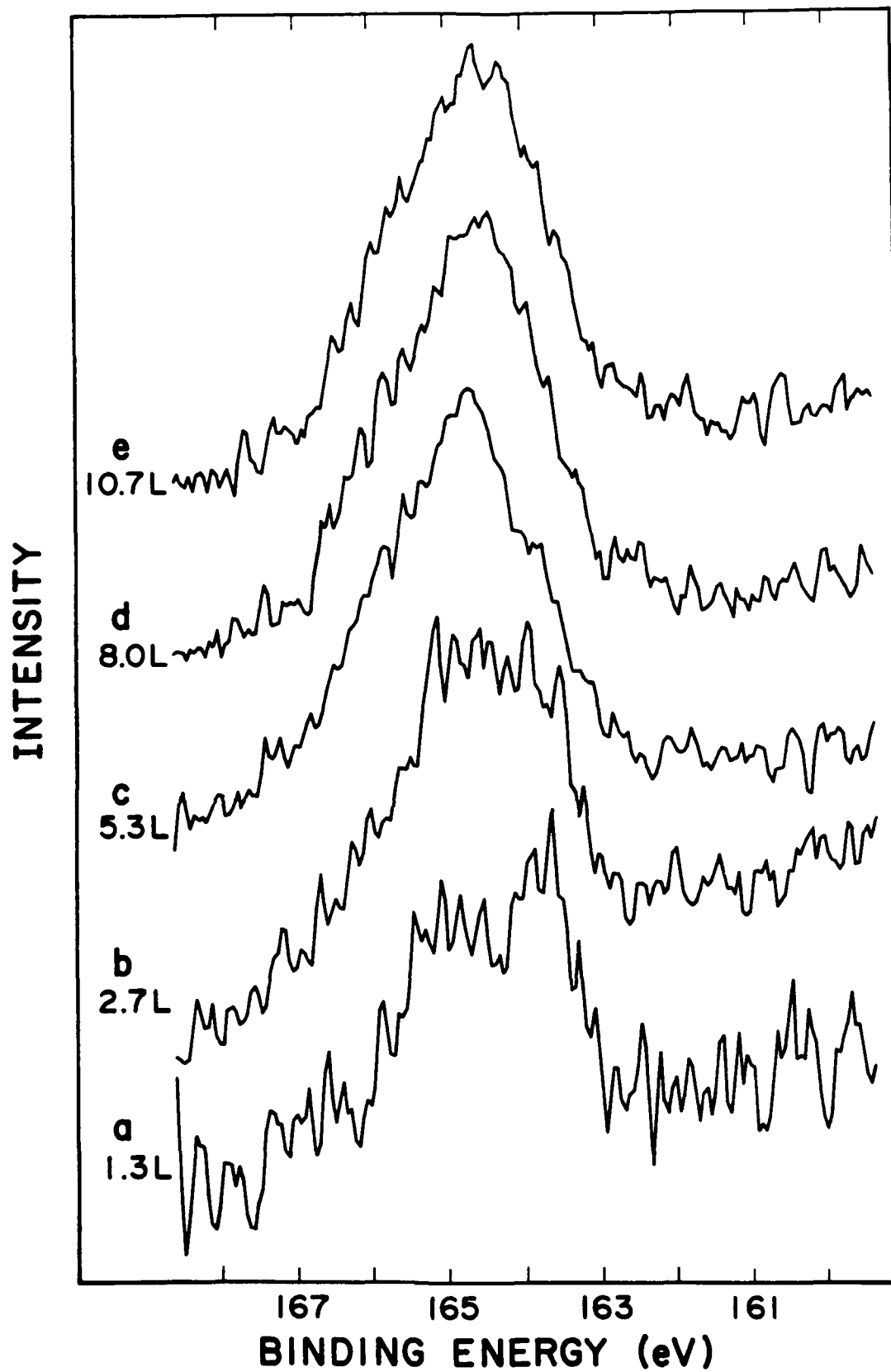


Figure 1

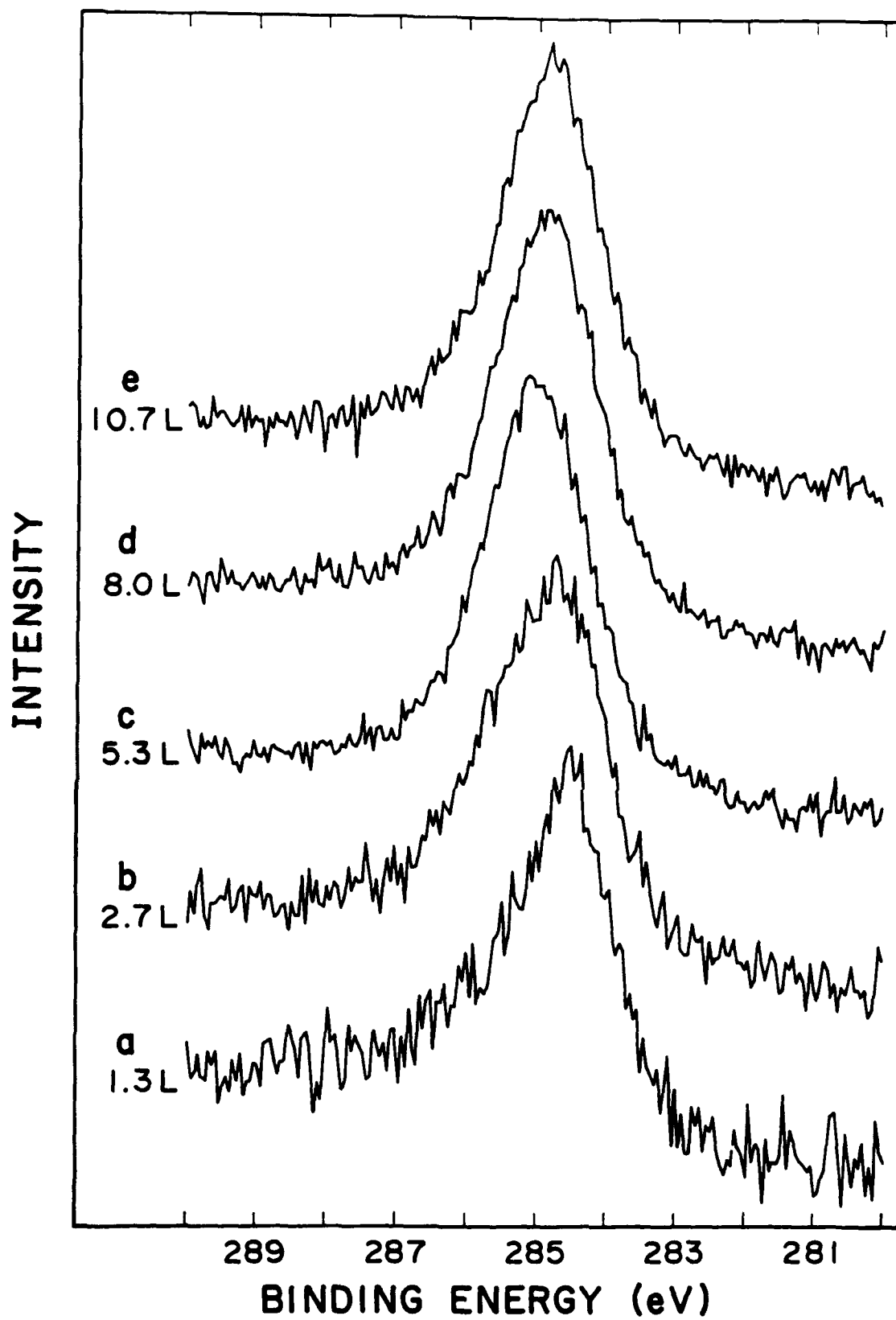


Figure 2

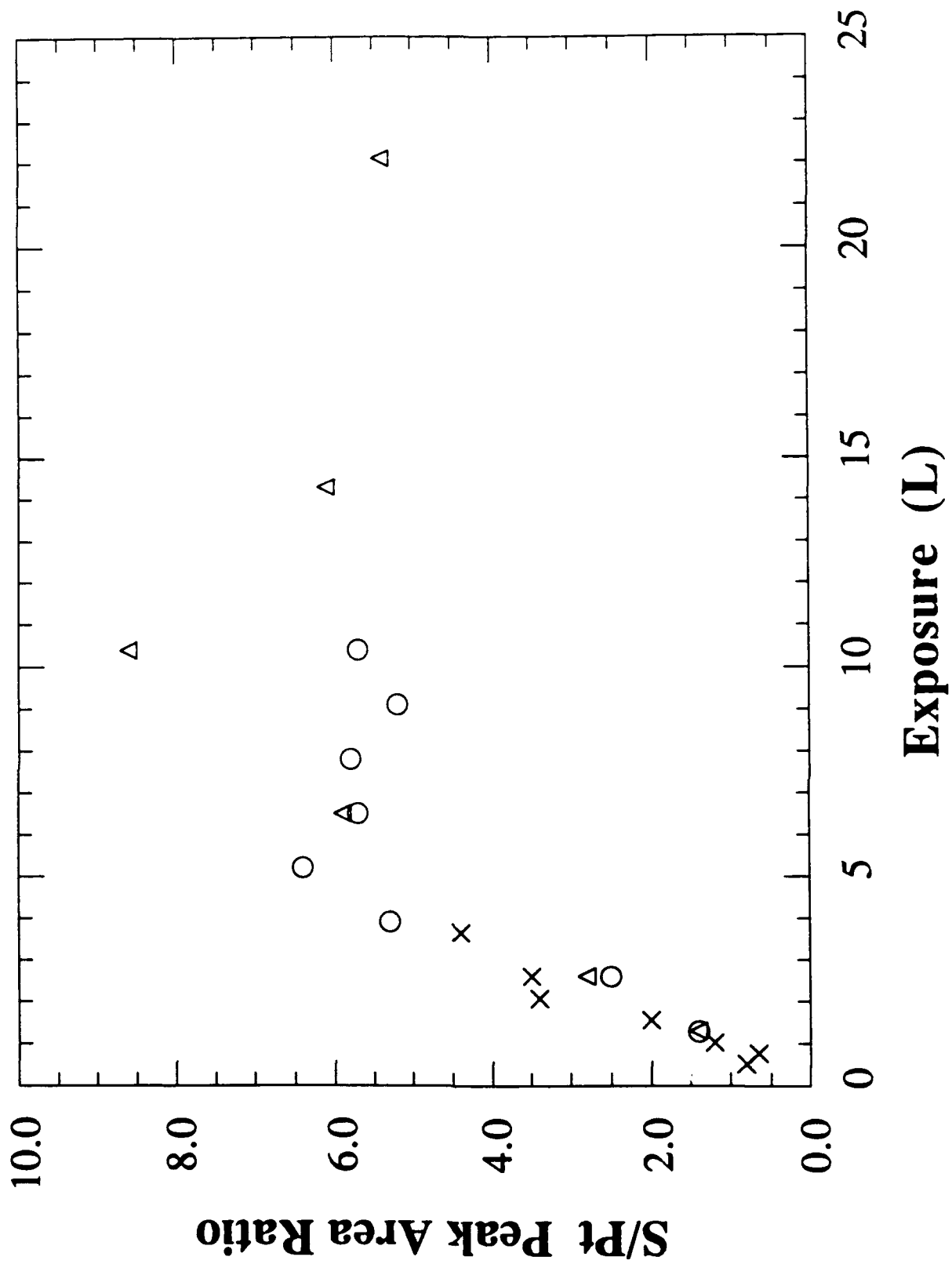


Figure 3

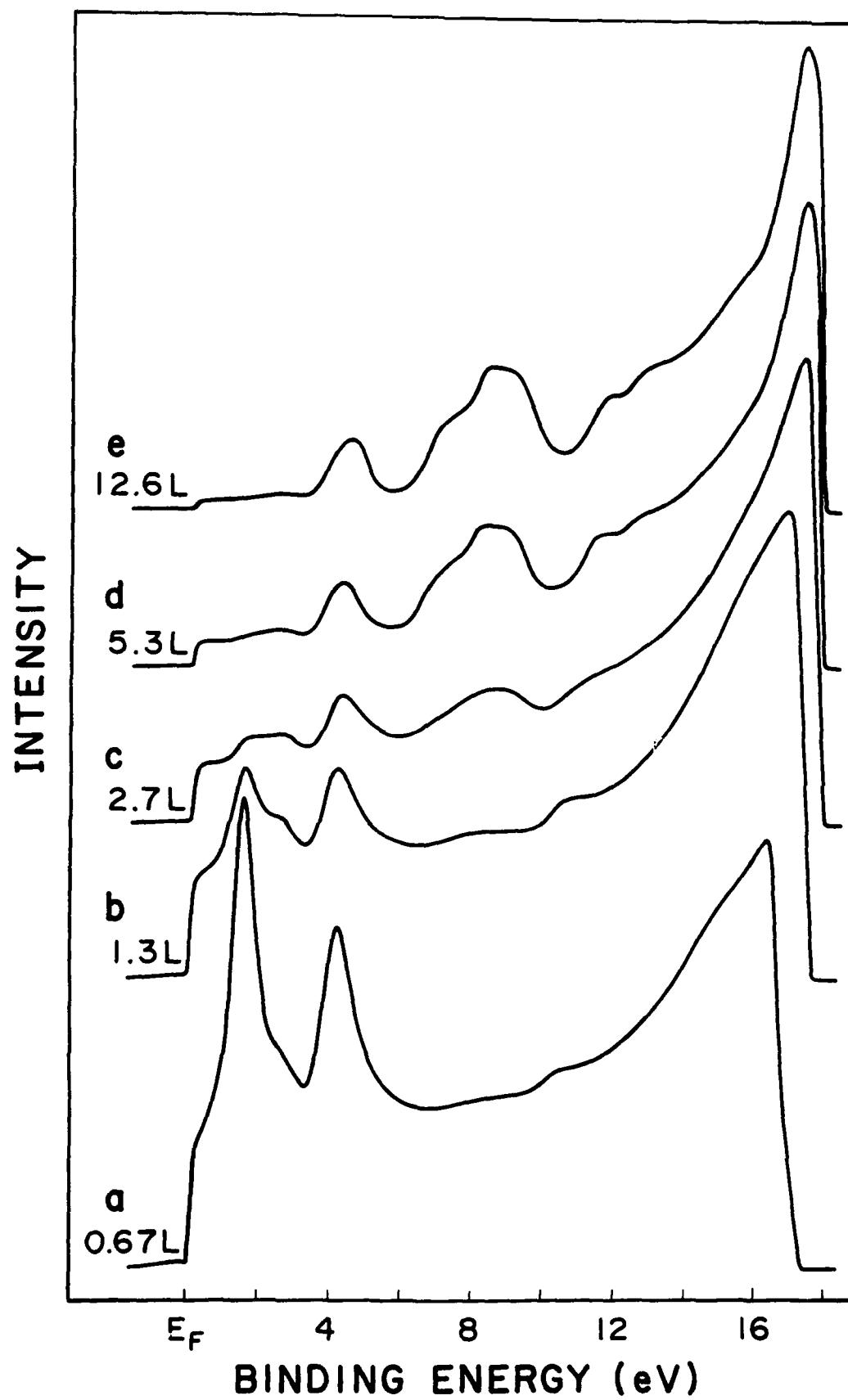


Figure 4

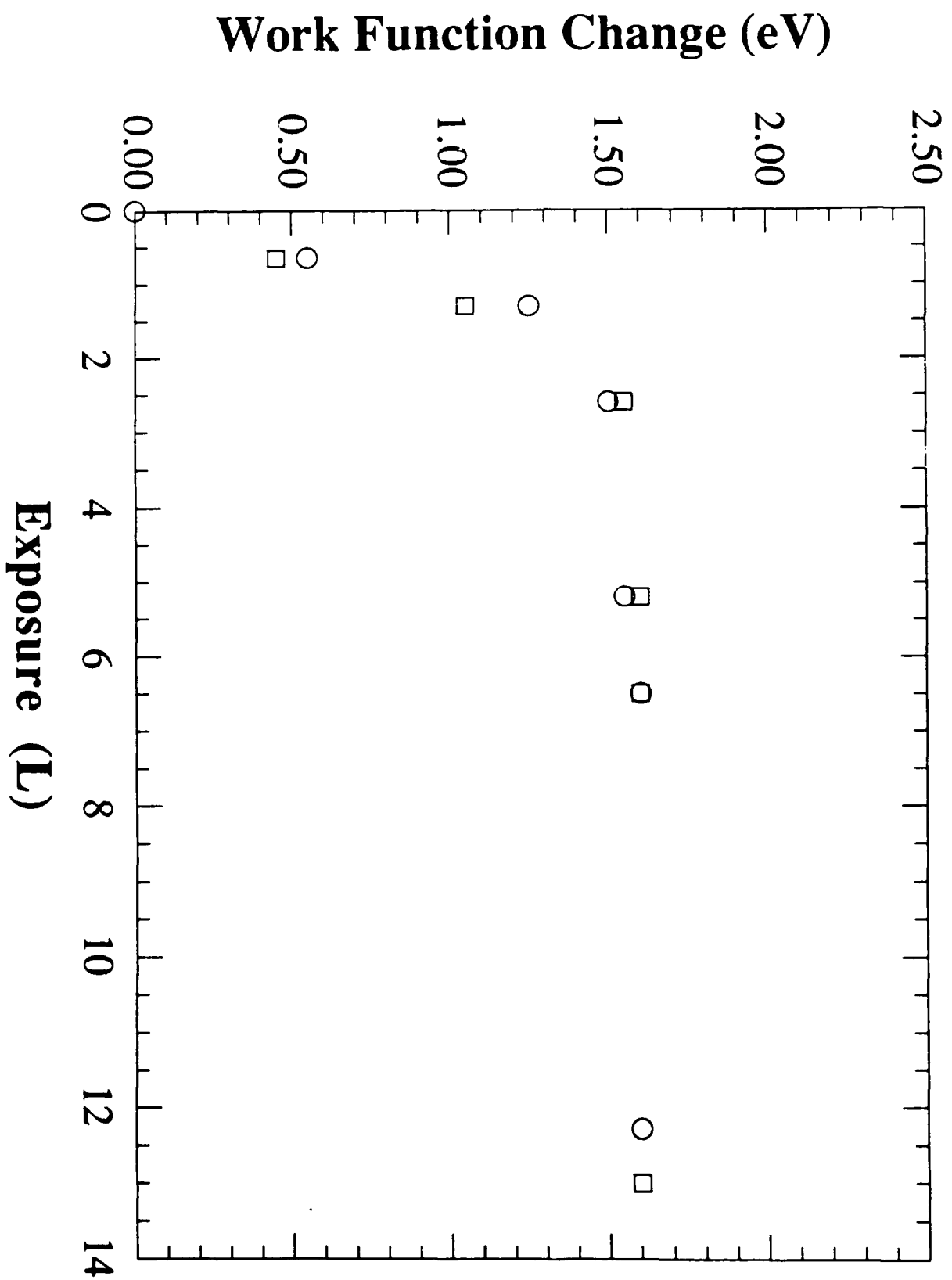


Figure 5

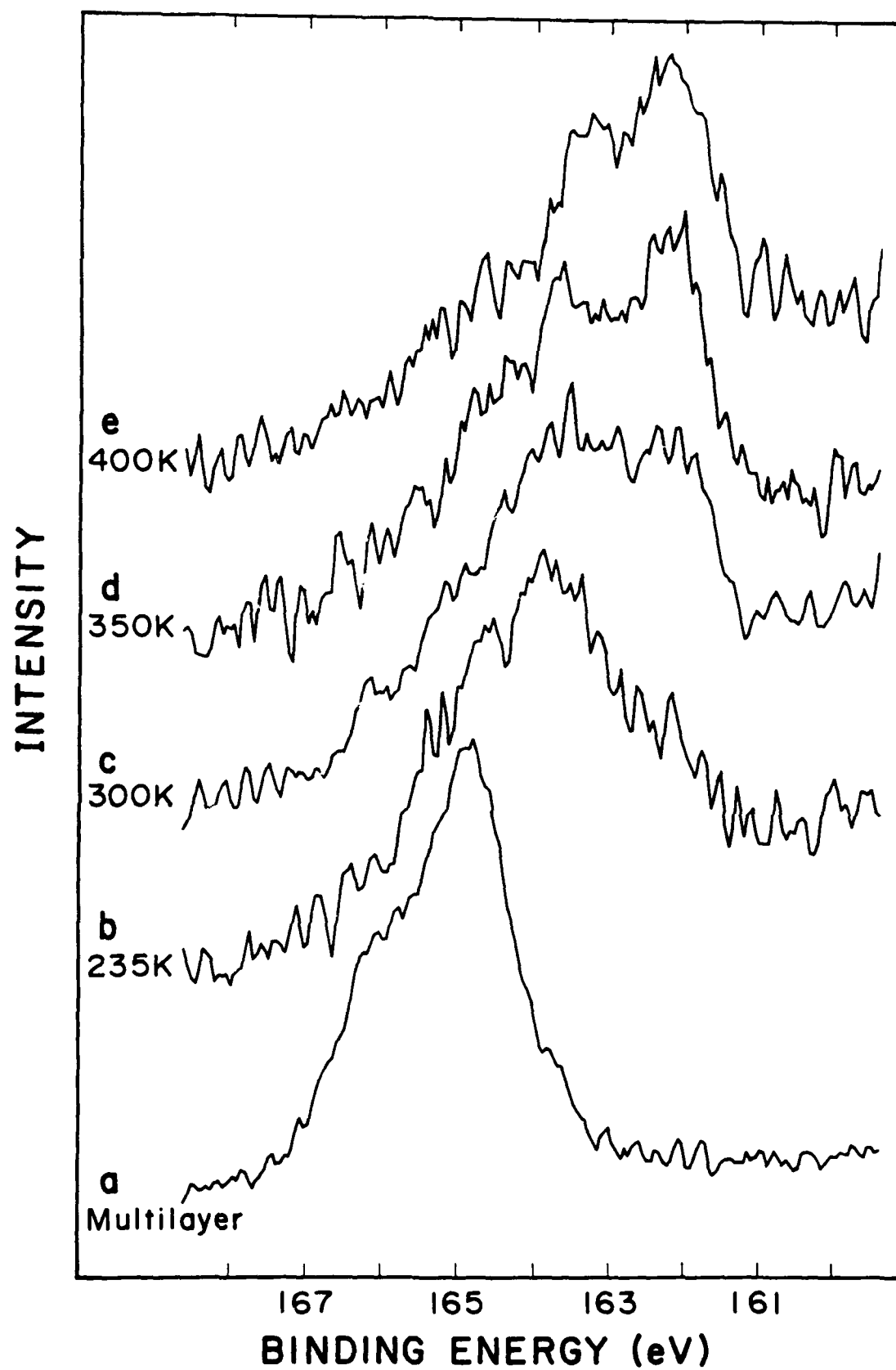


Figure 6

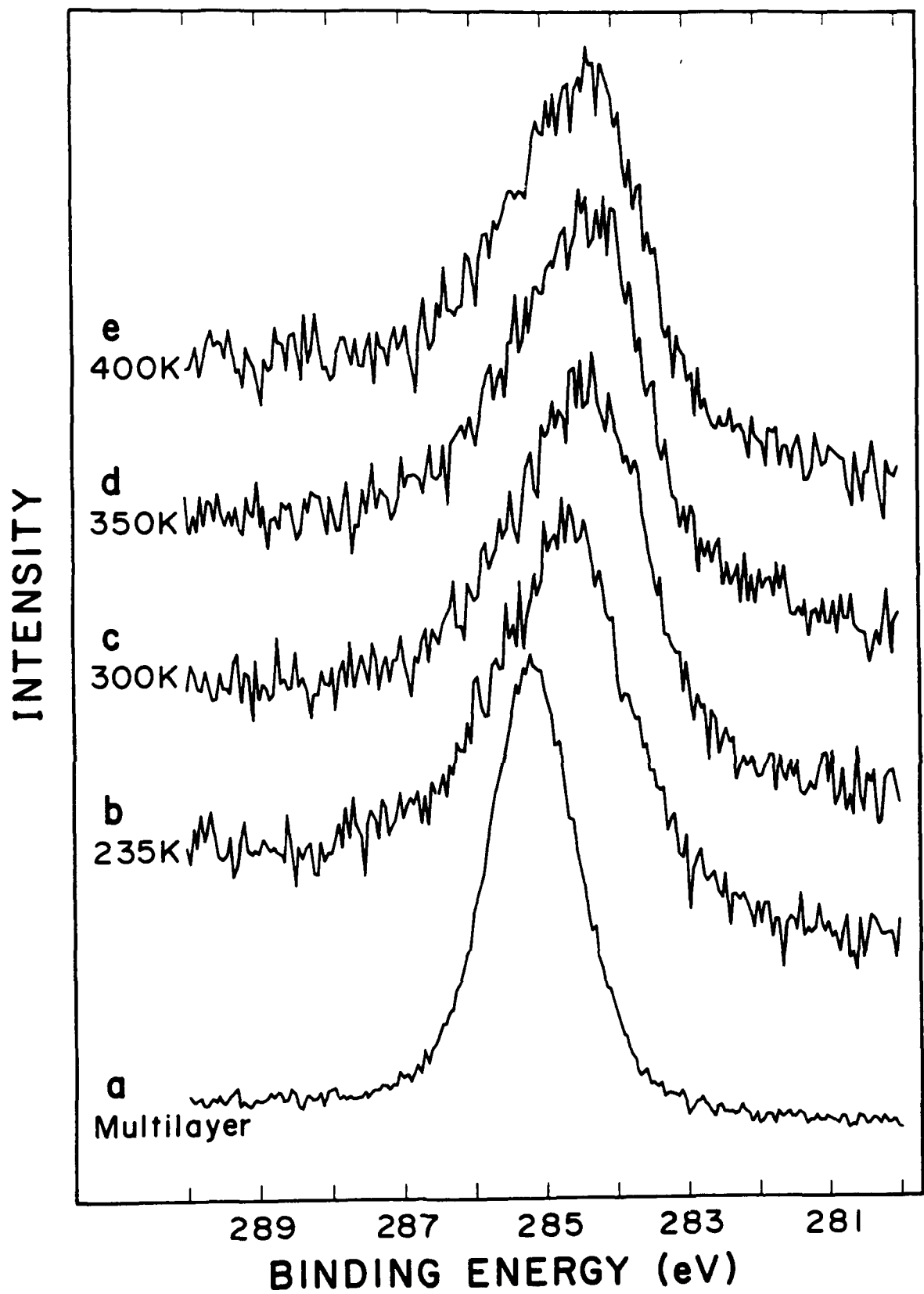


Figure 7

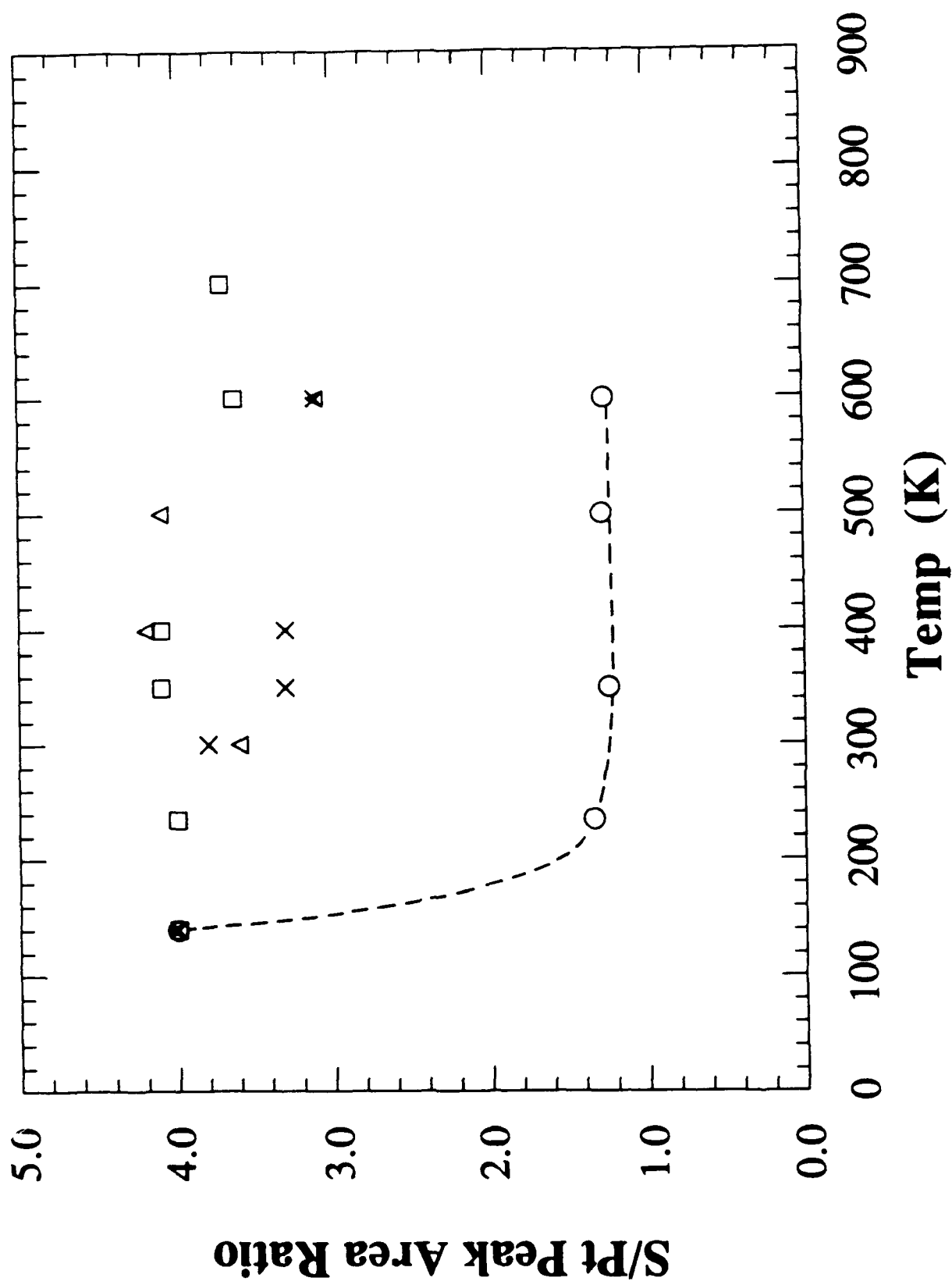


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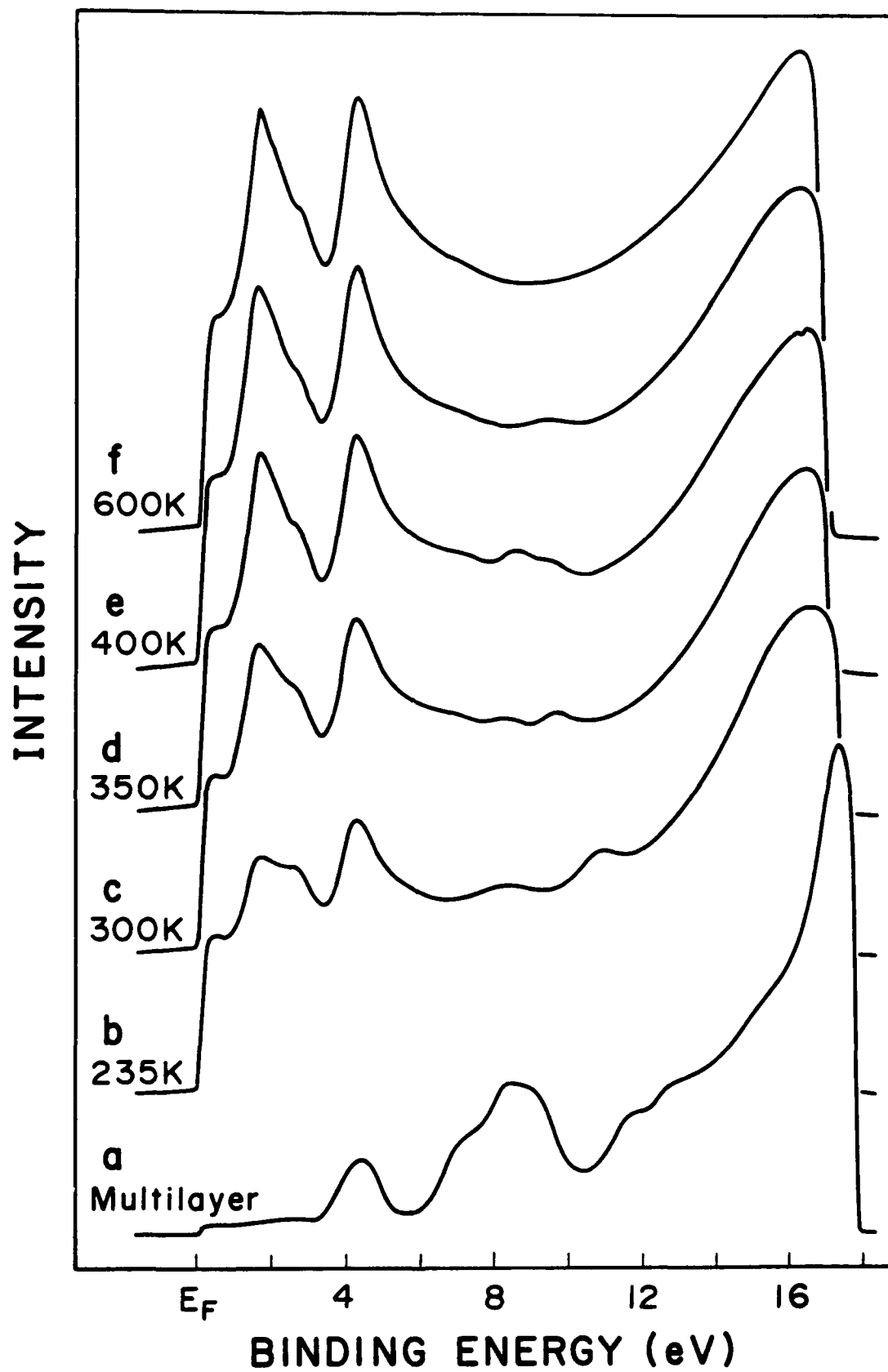


Figure 9

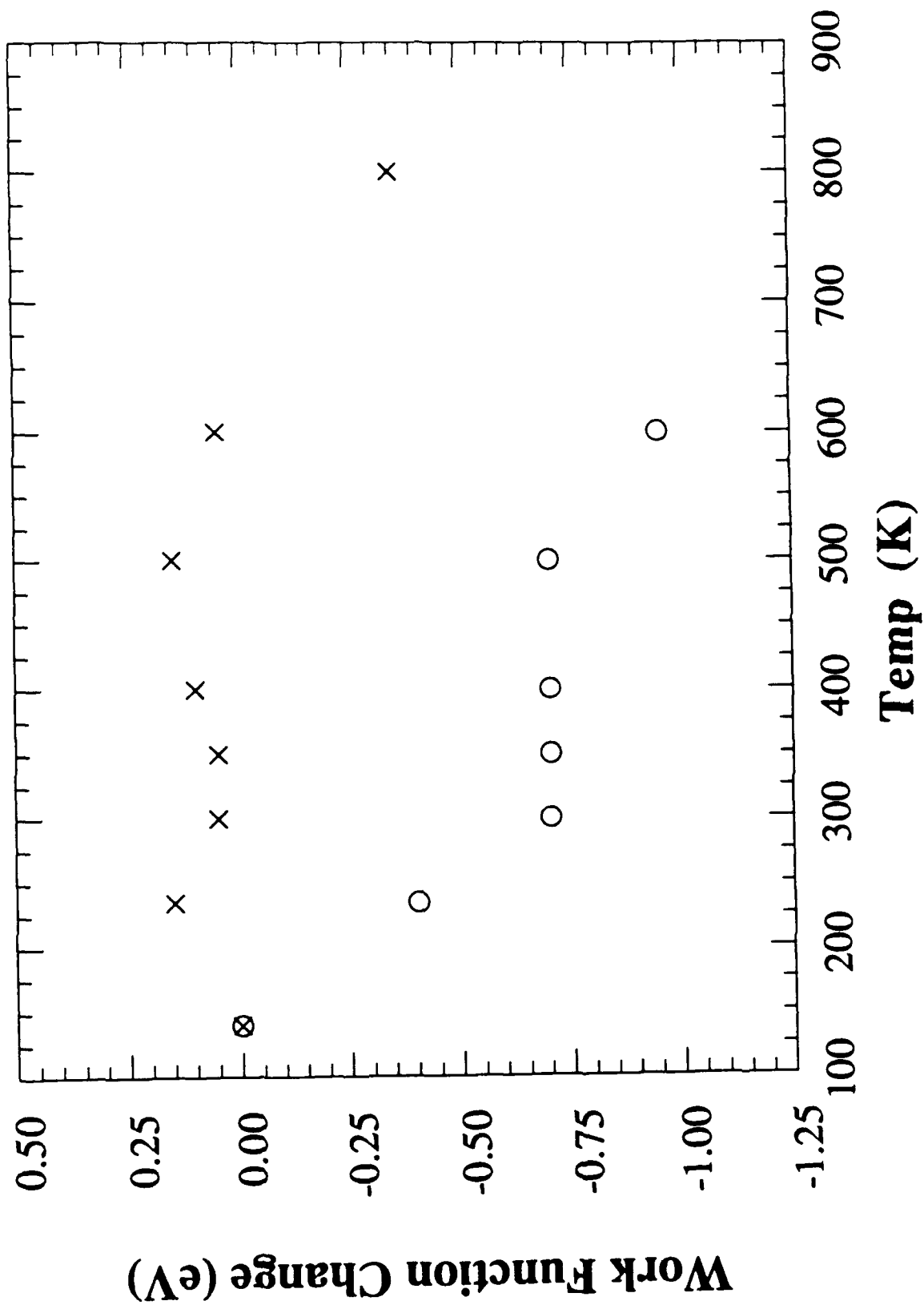


Figure 10

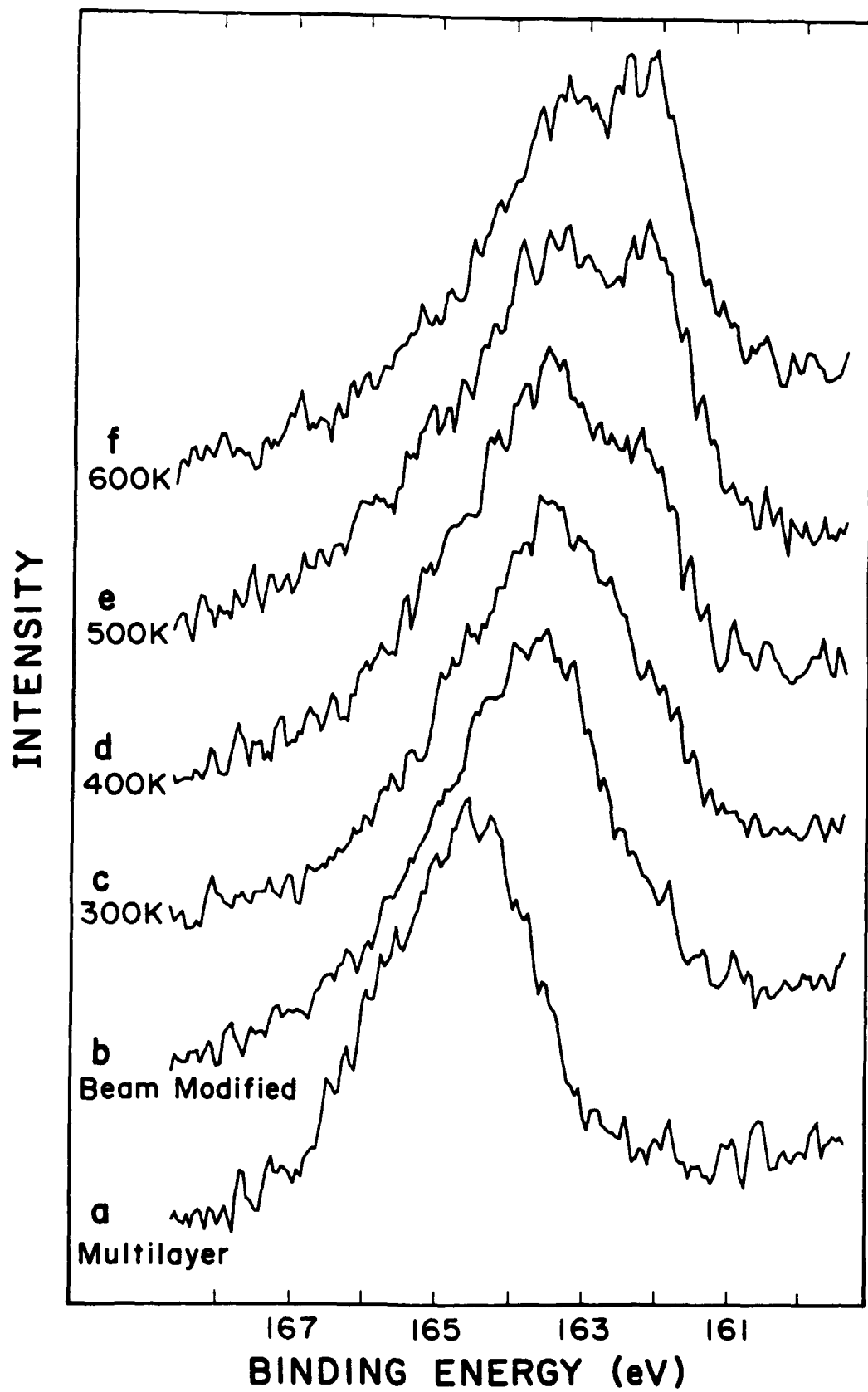


Figure 11

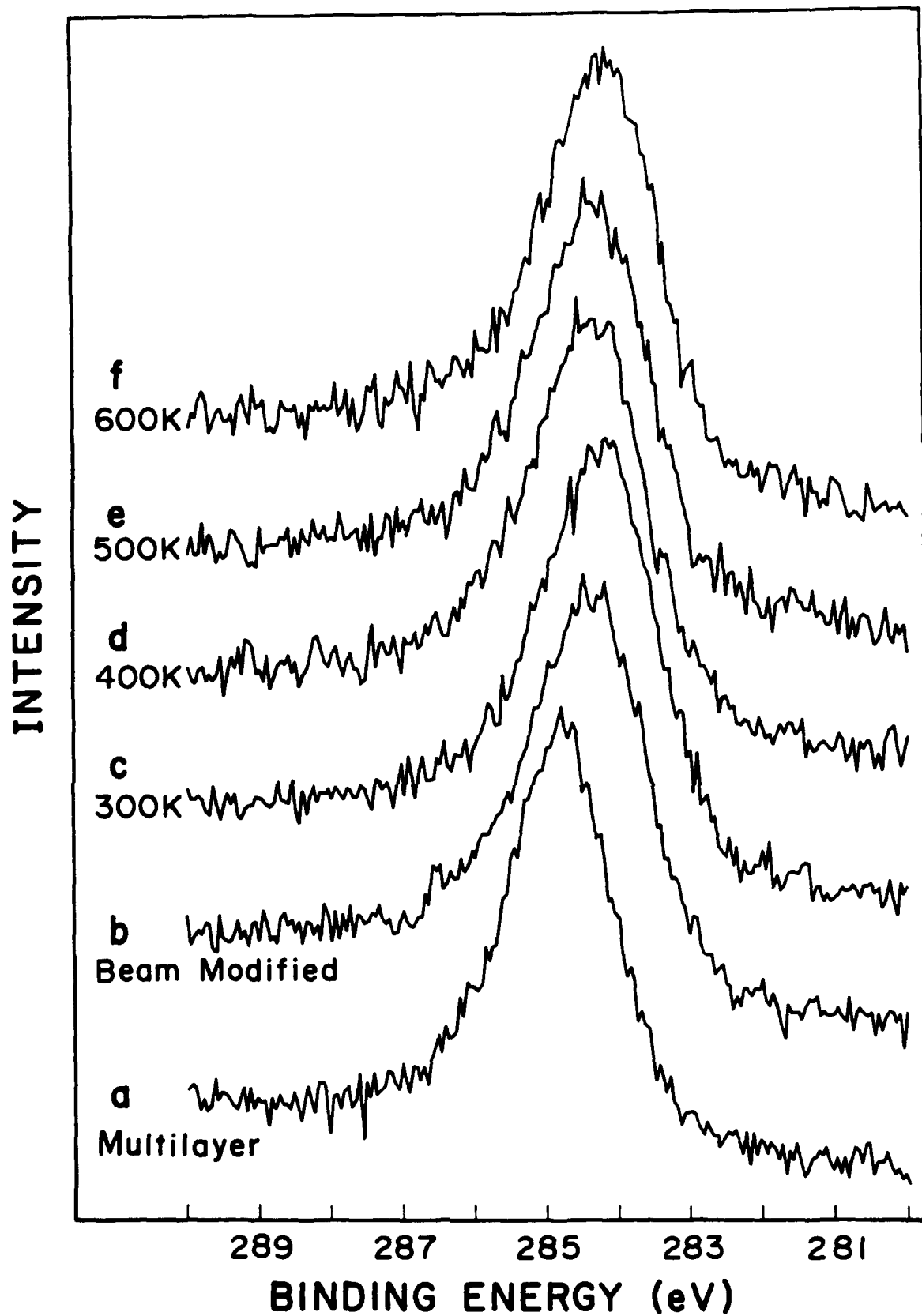


Figure 12

INTENSITY

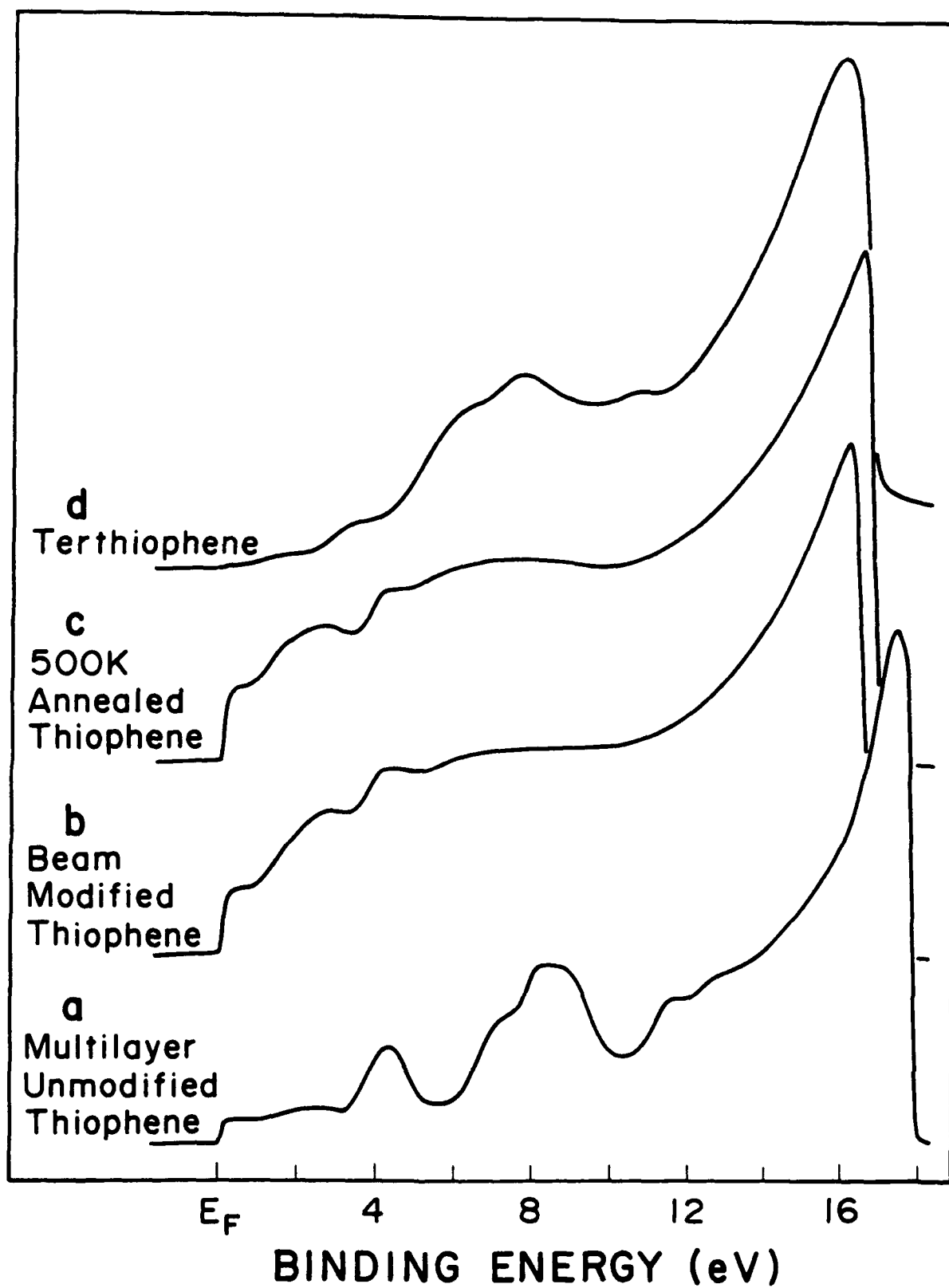


Figure 13